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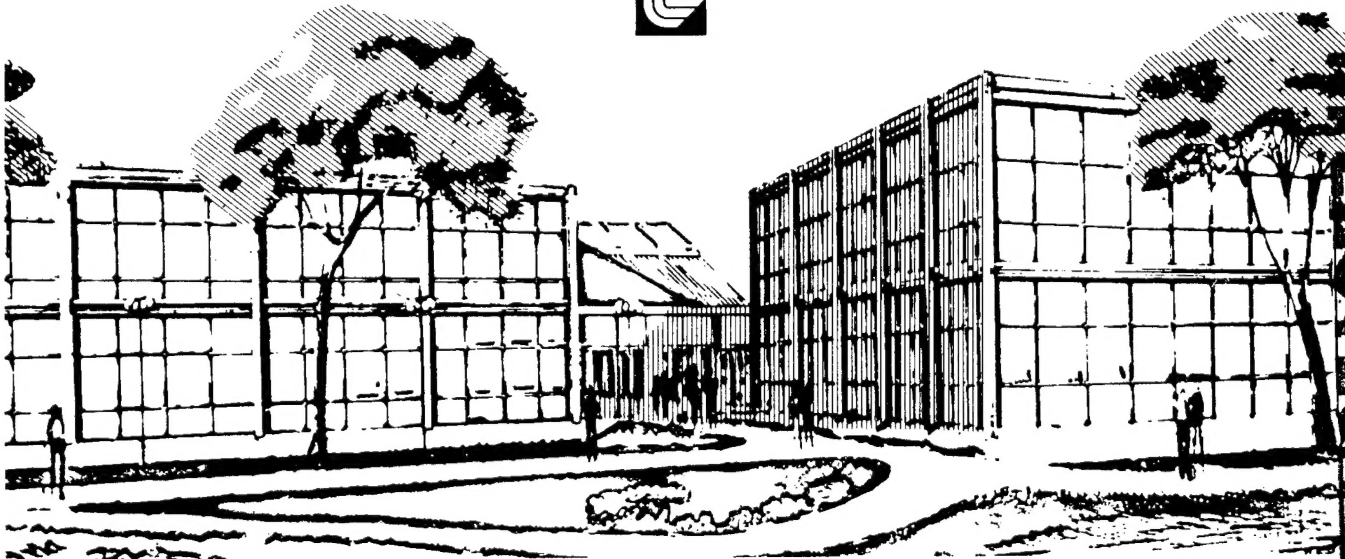
## **THE REACTION KINETICS OF PHENYL GLYCIDYL ETHER WITH 2,5-DIMETHYL-2,5-HEXANEDIAMINE**

J. A. Rinde, J. A. Happe, and H. A. Newey

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THE REACTION KINETICS OF PHENYL GLYCIDYL ETHER

WITH 2,5-DIMETHYL-2,5-HEXANEDIAMINE\*

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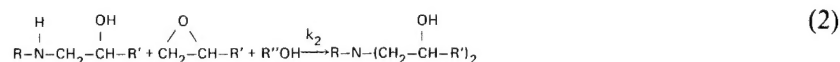
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## ABSTRACT

The reaction rate of phenyl glycidyl ether with the amine 2,5-dimethyl-2,5-hexanediamine has been measured in dimethyl sulfoxide solution at four temperatures from 46 to 100°C. Carbon-13 NMR was used to monitor the concentrations of reactants and products. Using this technique we were able to measure independently the reaction rates of both the primary and secondary amine hydrogens. The ratio of reaction rates  $k_1/k_2$  is 60:1, the largest ratio ever reported. The activation energy for either reaction is 13.7 kcal/mole. The reactions are catalyzed by hydroxyl groups, and the mechanism used to explain our data is consistent with those of previous workers.

## INTRODUCTION

The cure of epoxy resins with polyprimary amines proceeds by an addition reaction of the amine with the epoxide group and is catalyzed by hydroxyl groups.<sup>1</sup> The reaction can be illustrated, using monofunctional epoxies, as follows:

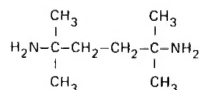


In the usual case, the epoxy resin is difunctional and the polyamine at least tetrafunctional, and the reaction leads to a crosslinked polymer. Also there is no evidence<sup>2</sup> for the tertiary amine (resulting from the reaction of one mole of ethylenediamine and four moles of phenyl glycidyl ether (PGE)) catalyzing the reaction of the epoxide group with the hydroxyl. The effects of amine and hydroxyl group structures in reactions 1 and 2 have been thoroughly investigated and summarized.<sup>1,3</sup>

Relatively few measurements of the ratio of reaction rates  $k_1$  and  $k_2$ , in Eqs. 1 and 2, are reported in the literature. For aliphatic primary amines, the ratio  $k_1/k_2$  was 1.5 for the reaction of ethylene oxide with monoethanol and diethanol amine.<sup>4,5</sup> For propylene oxide and *n*-butylamine<sup>4,5</sup> it was 2.05 and for diglycidyl ether of bisphenol A (DGEBA) reacted with *n*-butylamine or ethylene diamine<sup>6</sup> it was 2.0. For the aromatic amine methylene dianiline reacted with DGEBA<sup>7</sup> the ratio is reported to be from 7 to 12. This ratio is the highest previously reported.

An amine with a  $k_1/k_2$  ratio of 50 to 100 or larger could be of great practical value. An example would be a diepoxy resin-diprimary amine system that after being applied as a liquid would cure to a soluble fusible solid, stable for a long period of time, but on heating to a higher temperature would cure completely to a strong crosslinked structure. In this example, the first amine hydrogen forms a linear polymer when it reacts with the epoxy resin; and if the second amine hydrogen reacts slowly enough, this linear polymer would be stable until heated to a higher temperature where the second amine hydrogen would react and crosslink the system.

In this paper, we present measurements for  $k_1$  and  $k_2$  for the reaction of 2,5-dimethyl-2,5-hexanediamine (DMHDA) with PGE and show that the ratio  $k_1/k_2$  is 60:1. In a previous publication,<sup>8</sup> we showed that DMHDA when reacted with pure DGEBA epoxy resin does indeed yield a room-temperature-stable linear polymer. The compound DMHDA has the following structure:



Because of the steric hindrance of the methyl groups adjacent to the amine groups, one would expect the reactivity of the amine groups to be reduced. Indeed their reactivity is reduced about 40-fold over normal aliphatic amines, as measured by gel times with pure DGEBA epoxy resins.

The use of carbon-13 NMR to study the curing of the diglycidyl ether of bisphenol A with piperidine has been reported earlier.<sup>9</sup> In the present work, we used carbon-13 NMR to follow the progress of the reaction between PGE and DMHDA. The reactant molecules and various product molecules gave distinguishable spectra. Thus the concentration changes occurring during the reaction could be followed by monitoring selected NMR peak intensities. The peaks most convenient to use were those originating from methyl groups of reacted and unreacted DMHDA molecules.

## EXPERIMENTAL

The reaction of DMHDA with PGE was carried out in dimethyl sulfoxide (DMSO) solution at 1:1 stoichiometry (one amine hydrogen to one epoxide). A solvent was necessary to obtain good NMR spectra; DMSO was chosen because of its high boiling point, good solvent properties, and its NMR properties. Chloroform would have been a better solvent but could not be used at these reaction temperatures. The DMSO partially failed as a solvent at the completion of the first reaction when some precipitate formed. This disappeared with time as the second reaction proceeded.

The reactants were preheated to 40 to 60°C and the materials were weighed directly into a glass reaction vessel where they were mixed at zero time. The reaction vessel was placed in a constant temperature bath at 60, 80, or 100 ± 0.01°C, and the first sample was removed. Samples of 4.5 ml were removed with a preset pipet and placed directly into a 12-mm NMR tube, which was sealed to prevent moisture pickup or evaporation. Tubes were cooled in ice water to stop the reaction and were taken immediately for NMR analysis. Some samples remained in ice water for 1 to 2 h before being run in the NMR. During the NMR run, the sample temperature was from 45 to 55°C. Water concentration, determined by analysis of samples taken from the NMR tubes, was used as the initial hydroxyl concentration.

Carbon-13 NMR spectra were obtained at 15.075 MHz on a multinuclear spectrometer designed in this laboratory. A Nicolet\* model NT 440, broad-band variable-temperature probe was used with 12-mm NMR tubes. The spectrometer was operated in the pulse mode with an external <sup>19</sup>F lock and noise decoupling of protons. The 90° pulse width was 32 μs. To obtain a spectrum, we accumulated 1000 transients in a 1024-channel Fabri-Tek memory using a single phase detector. A 21-μs pulse and a 2-μs recycle delay were used. A 0.5-Hz line-broadening function was applied to the accumulated signal for sensitivity enhancement and then it was Fourier transformed, using a Varian 620/L 100 minicomputer. The spectral width was 2500 Hz (165.84 ppm) divided into 1024 points. A 4-pole, 2.5-kHz Butterworth filter was used in accumulating the data.

Chemical shifts were measured relative to the carbon-13 signal of the DMSO solvent and converted to the tetramethyl silane (TMS) scale by using 40.48 ppm as the downfield shift for DMSO relative to internal TMS.

The carbon-13 combined spectrum of PGE and DMHDA in dimethyl sulfoxide is shown in Fig. 1, taken at the time of mixing and before significant reaction had occurred. The chemical shifts (see Fig. 1) for the reactants are in agreement with those for compounds similar to PGE.<sup>9</sup>

\*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

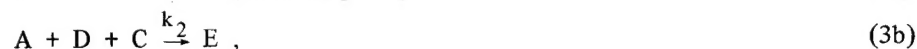
As polymerization progresses, new peaks appear in the carbon-13 spectra of reacting mixtures. To help in the assignment of these peaks, two product molecules were prepared. The first was formed by reacting only the primary amine hydrogens using a 2:1 PGE:DMHDA mixture. The product was recrystallized from  $\text{CHCl}_3$ . The second product was prepared by carrying the polymerization reaction to completion using a 4:1 PGE:DMHDA mixture. The spectra of these two products and the shifts are shown in Fig. 2.

Proton-coupled spectra were used to help assign the NMR peaks, and both DMSO and  $\text{CHCl}_3$  were used as solvents. In the  $(\text{PGE})_4\text{-DMHDA}$  product, the two "b" carbons appear to be nonequivalent, and in the proton-coupled spectrum these carbons are doublets. Also, the two "c" carbons appear to be nonequivalent and to give proton-coupled triplets.

The methyl peak of DMHDA was most convenient for monitoring the progress of the polymerization reaction. Reactions of the primary-amine hydrogen shift this carbon resonance 3.4 ppm to higher field. Reaction of the secondary-amine hydrogen gives a new peak 5.8 ppm upfield from the unreacted peak position at 30.3 ppm (vs TMS). Peak heights were used to monitor concentration changes. Small changes in system gain or magnet homogeneity were compensated for by monitoring the DMSO carbon-13 peak amplitude.

#### KINETICS OF THE DMHDA-EPOXY REACTION

The hydroxyl-catalyzed reaction of an epoxy resin with an amine is shown by Eqs. (1) and (2) and represents a third-order reaction that is first order in each reactant. Reactions 1 and 2 can be written in the following form:



where A is the PGE concentration in equiv/litre, B is that for DMHDA, and C is that for ROH. From reaction stoichiometry,  $dA = dB$  and, therefore,

$$A_0 - A = B_0 - B , \quad (4)$$

and

$$B = B_0 - A_0 + A , \quad (5)$$

where  $A_0$  and  $B_0$  are initial concentrations of A and B. Since the reaction produces one hydroxyl group for every A consumed, the ROH concentration is

$$C = C_0 + (B_0 - B) , \quad (6)$$

where  $C_0$  is the initial ROH concentration.

For reaction (3), which is first order in each reactant, we have

$$-dA/dt = k[A][B][C] . \quad (7)$$

Substituting (5) and (6) into (7) yields

$$-dA/dt = k[A][B_0 - A_0 + A][C_0 - A + A_0] . \quad (8)$$

This expression can be integrated by means of partial fractions to yield the rate equation:

$$A_2 \ln A_0/A + B_2 \ln B/B_0 + C_2 \ln [C_0/(C_0 + A_0 - A)] = kt , \quad (9)$$

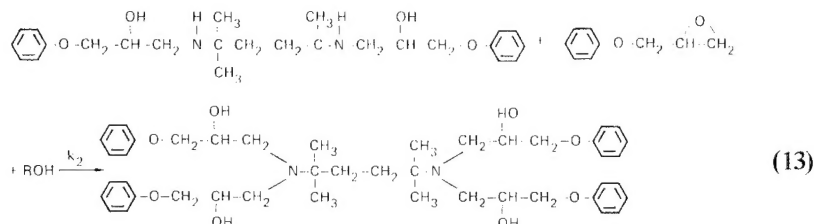
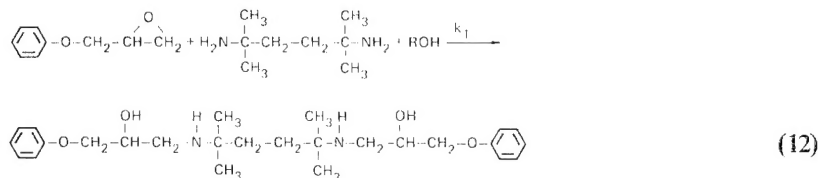
where

$$A_2 = 1/(C_0 B_0 + A_0 B_0 - A_0 C_0 - A_0^2) , \quad (10)$$

$$B_2 = A_2(A_0 + C_0)/(C_0 + B_0) ; \quad C_2 = A_2(A_0 - B_0)/(C_0 + B_0) . \quad (11)$$

If this mechanism is correct, plots of the left hand side of Eq. (9) vs time will yield a straight line whose slope will equal  $k$ .

In our work, we used a diamine, and two assumptions were made to apply Eq. (9) to our data. The first was that both of the primary amine hydrogens of the diamine react at the same rate. The second was that the rate of reaction of the secondary amine hydrogens is much less than that of the primary amine hydrogens,  $k_2 \ll k_1$ . If these assumptions are correct, then we can treat the reaction of the primary and secondary amine hydrogens as separate reactions occurring sequentially in time.



To apply Eq. (9) to the above two reactions, we note that the concentration of PGE and hydroxyl groups are calculated from the amounts of material present. Since we are treating the reaction of the primary amine separately, the concentration of primary amine is one-half the total amine concentration. Therefore, the loss of the carbon-13 peak ( $\text{NH}_2$ ) at 30.3 ppm corresponds to loss of one-half the initial total amine-hydrogen concentration. In the secondary amine reaction, the starting concentrations of PGE and amine are the initial concentrations minus the amount reacted; and the hydroxyl concentration is the initial concentration plus the amount produced in the first reaction [Eq. (3a)].

For the first reaction, the amine concentration at any time is derived from the carbon-13 peak-height data by the equation

$$B = B_0(H/H_0) , \quad (14)$$

where  $B_0$  is the amine-hydrogen concentration,  $H$  is the height of the 30.3 ppm peak at time  $t$ , and  $H_0$  is the height of the initial peak. The concentration of PGE at any time is calculated by using Eq. (4).

The application of Eq. (9) to our data has been programmed on a PDP-8i computer. Inputs are the initial concentrations of reactants and the peak height vs time data. Outputs are the coefficients of Eq. (9), concentrations vs time, and  $kt$ . For these data, we receive a printout, a plot of the data, and the least-squares slope ( $k$ ) of the best straight line through the data.

As an example, we will discuss our data taken at  $100^\circ\text{C}$  for the reaction of PGE + DMHDA in DMSO. We reacted the materials at 1:1 stoichiometry (one amine hydrogen to one epoxide) in DMSO solution. Figure 3 shows two examples of the carbon-13 NMR spectra obtained during this kinetic run. The lower spectrum (b) represents the combined spectra for all the materials present at zero time. Several peaks could be used to follow this reaction, but the sharp peak at 30.3 ppm is the most intense and shows the largest change with concentration of the amine DMHDA. As a result, this peak was used to follow the reaction of the primary amine hydrogens with PGE. The spectrum in Fig. 3(a) shows the

resulting combined spectra after 23 h at 100°C. Here the peak at 30.3 ppm is absent, and two new peaks have developed at 26.9 ppm and 24.5 ppm. These peaks are due to the secondary amine and tertiary amine, respectively. Other peaks appear but will not be discussed further, because the peaks in the range from 20 to 40 ppm are of greater interest. A series of these peaks, taken at various times, is presented in Fig. 4. These show the progressive disappearance of the primary amine peak (P), the growth of the secondary amine peak (S), and its subsequent decrease as the tertiary amine peak (T) grows in height. The decrease in the 26.9-ppm peak was used to follow the reaction of the secondary amine hydrogens with PGE.

Figure 4 shows the primary peak is completely absent after 2 h at 100°C, the secondary amine peak is very intense, and no tertiary amine peak can be detected above the background noise. This demonstrates that the reaction of the primary amine hydrogens is complete before any significant reaction of the secondary amine hydrogen takes place. Thereafter, the peak for the secondary amine decreases slowly with time and the peak for the tertiary amine grows.

The results plotted in Fig. 5 as peak height vs time show all our data obtained at 100°C. The scatter in the secondary amine peak at 1.5 to 2.25 h is probably because of some precipitate observed in the NMR tubes. The noise level in the NMR spectra is 20 to 25 units and, therefore, no reliable data are obtained below this point. By plotting the concentrations of primary amine, secondary amine, and PGE vs time, we see that the amine and PGE concentration curves are parallel, showing that one amine is reacting quantitatively with one PGE.

To determine if Eq. (9) represents our data at 100°C, we enter the starting concentrations into Eq. (9), which then reduces to

$$-0.4765 \ln 1.9393/A - 0.8613 \ln B/0.9711 - 0.3849 \ln \left( \frac{0.228}{2.1673 - A} \right) = kt \quad (15)$$

Values for A, B, and t are substituted into Eq. (15), and values for kt are calculated. If this equation represents our data, then a plot of the left side of Eq. (15) vs time will yield a straight line of slope k. Such a plot, presented in Fig. 8(a), indeed yielded a straight line for the data points for the first reaction.

To apply Eq. (9) to the reaction of the secondary-amine hydrogen with PGE, we must reevaluate the constants, using new values for the starting concentrations of amine, PGE, and OH. We must also redefine zero time for the second reaction. In this case, we used 2 h for the zero time point. The equation for the second reaction is:

$$158.02 \ln 0.9682/A + 157.81 \ln B/0.9711 - 0.2126 \ln \left( \frac{1.1991}{2.1673 - A} \right) = kt \quad (16)$$

This data also yields a straight line plot as shown in Fig. 6(a). The slopes (k) of these lines are 1.892 and 0.0317 [(equiv/litre)<sup>-2</sup>h<sup>-1</sup>] for the first and second reactions, respectively. In this case, the reaction rate of the primary amine hydrogen is 59.6-times faster than that of the secondary amine hydrogen.

Kinetics plots of the data at 80, 60, and 46°C are shown in Fig. 6(b) to (d). These third-order plots show good straight-line fits of the data. Rate constants from all these curves are given in Table 1. The ratio of reaction rates at these three temperatures is nearly constant and ranges from 59 to 66. Within the limits of the data, no trend in variation of the ratio  $k_1/k_2$  with temperature can be inferred.

The variation of  $k_1$  and  $k_2$  with temperature is shown in Fig. 7 (an Arrhenius plot). The data fall on two almost parallel straight lines with the exception of the 46°C data, with activation energies of 13.3 and 14.0 kcal/mole. These values were obtained from a least-squares fit of the data at 60 to 100°C. However, because of the uncertainty in the carbon-13 peak-height measurements, these values must be viewed as equal. If the 46°C data had been used in calculating the activation energy from the  $k_1$  data, the value would have been

TABLE 1. Rate constants for the reaction of 2,5-dimethyl-2,5-hexanediamine (DMHDA) with phenyl glycidyl ether (PGE) in dimethyl sulfoxide solution.

Temperature (°C)	$k_1$ [(equiv/litre) <sup>-2</sup> h <sup>-1</sup> ]	$k_2$ [(equiv/litre) <sup>-2</sup> h <sup>-1</sup> ]	$k_1/k_2$
100	1.892	0.0317	59.6
80	0.669	0.0112	59.6
60	0.219	0.00331	66.1
46	0.0567	—	—

15.0 kcal/mole. Because the 46°C kinetic run was obtained by a different experimental procedure and because of the uncertainty in the correctness and constancy of the temperature value, we have not included it in this activation energy calculation. An activation energy value of 13 to 14 kcal/mole is consistent with results of Parker *et al.*,<sup>10-14</sup> for the reaction of benzylamine with various monoepoxy compounds in several solvents. They found  $E_a$  values in the range from 10.9 to 18.6 kcal/mole. Smith<sup>1</sup> reports values of 13.0 to 15.6 kcal/mole for the activation energy of DGEBA reacting with amine in the presence of various additives. Recent measurements<sup>15</sup> on commercial, dicyandiamide-cured, epoxy resins yielded a somewhat higher  $E_a$  value of 20.7 kcal/mole.

## DISCUSSION

If the results presented above are to have a technological impact, then at least two problems must be overcome. The first involves the cost of materials compared to the value of the product produced. In the present case, DMHDA is expensive; however, its cost will be reduced substantially as volume increases. The second problem is to demonstrate that the new materials either perform better than existing materials in fabrication processes or have better mechanical or physical properties.

In our previous publication,<sup>8</sup> we showed that the observed high ratio of  $k_1/k_2$  for the reaction of DMHDA with the model epoxy resin PGE in DMSO solution did translate into unique properties when DMHDA was reacted with pure DGEBA-epoxy resin. For example, processing properties were improved for wet filament-winding applications and yielded mechanical properties that were very good. In addition, the glass transition temperature of the cured resin was unusually high for an aliphatic-amine-cured epoxy resin. However, the most impressive results were the formation of a room-temperature-stable, linear (non-crosslinked) polymer and the demonstration that this resulted in room-temperature-stable prepreps (preimpregnated products). Since that publication, we have extended our measurements on the neat resin system DGEBA/DMHDA and have shown that it is stable for one year at room temperature if protected from moisture. However, during this time some reaction does take place; the molecular weight of the linear polymer increases, but crosslinking does not take place, as shown by its solubility in chloroform and DMSO.

It is interesting that the activation energy of the primary and secondary amine hydrogens is the same. This means that the reduction in reaction rate of the secondary amine hydrogen is due only to the steric hindrance of the methyl groups. This effect indicates that a further increase in the ratio  $k_1/k_2$  could be obtained by replacing one or more of the methyl groups by ethyl or larger substitutes. This would lead to materials with greater room-temperature stability or even some stability at elevated temperatures. Complete cure (crosslinking) could still be achieved at temperatures below 150°C.

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## FIGURE CAPTIONS

Fig. 1. Carbon-13 NMR spectrum of PGE + DMHDA, showing chemical shifts (numbers in ppm above peaks) measured relative to the TMS scale (1 ppm = 15.08 Hz).

Fig. 2. Carbon-13 NMR chemical shifts (numbers in ppm above peaks) of the reaction products of (a) two PGE molecules with one DMHDA and (b) four PGE molecules with one DMHDA.

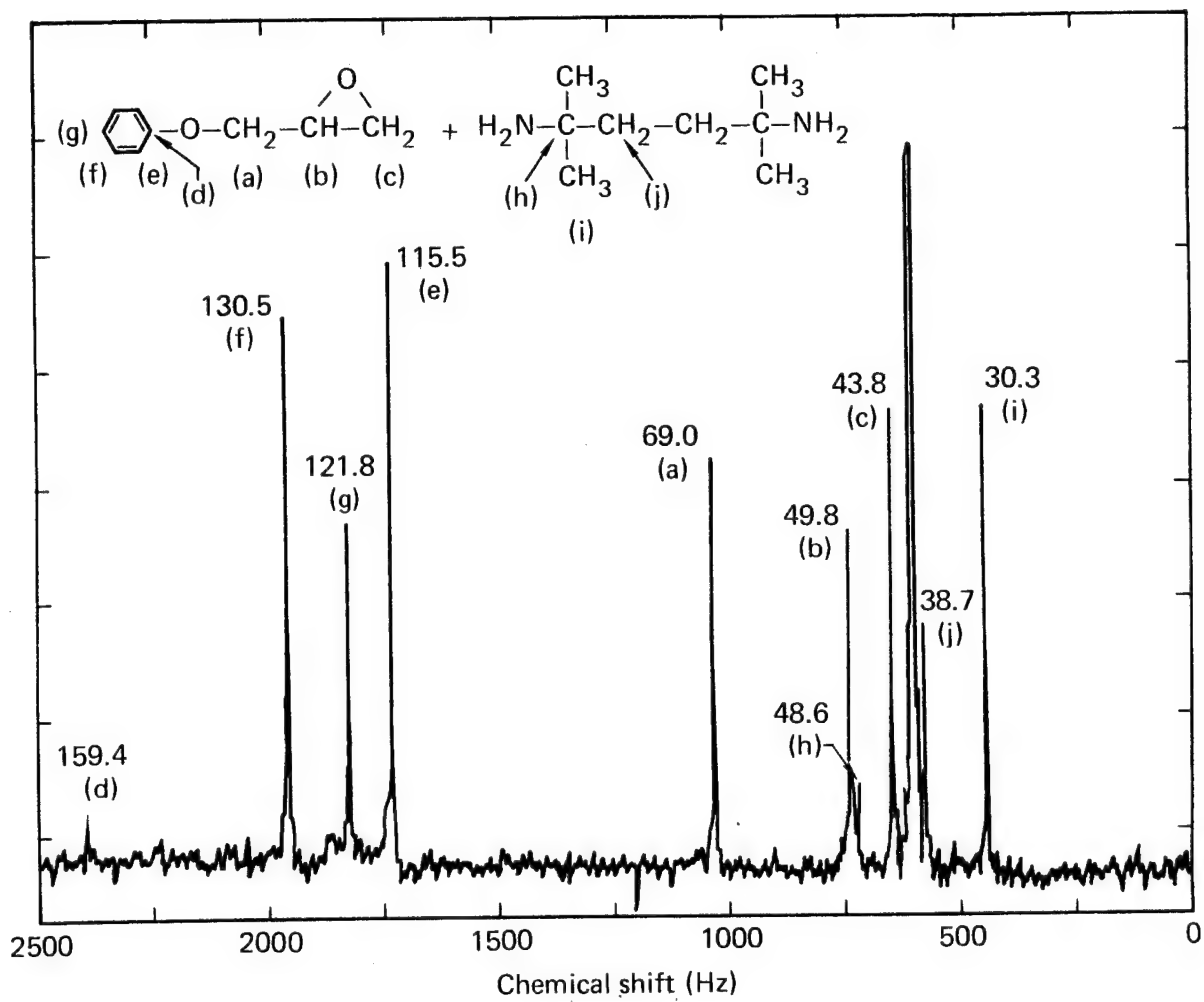
Fig. 3. Carbon-13 NMR spectra of mixture of DMHDA and PGE after reaction times of 0 and 23 h. Peaks corresponding to primary (P), secondary (S), and tertiary (T) amines are identified.

Fig. 4. Carbon-13 NMR peak heights corresponding to primary (P), secondary (S), and tertiary (T) amines for DMHDA + PGE in DMSO at 100°C at various times (hours).

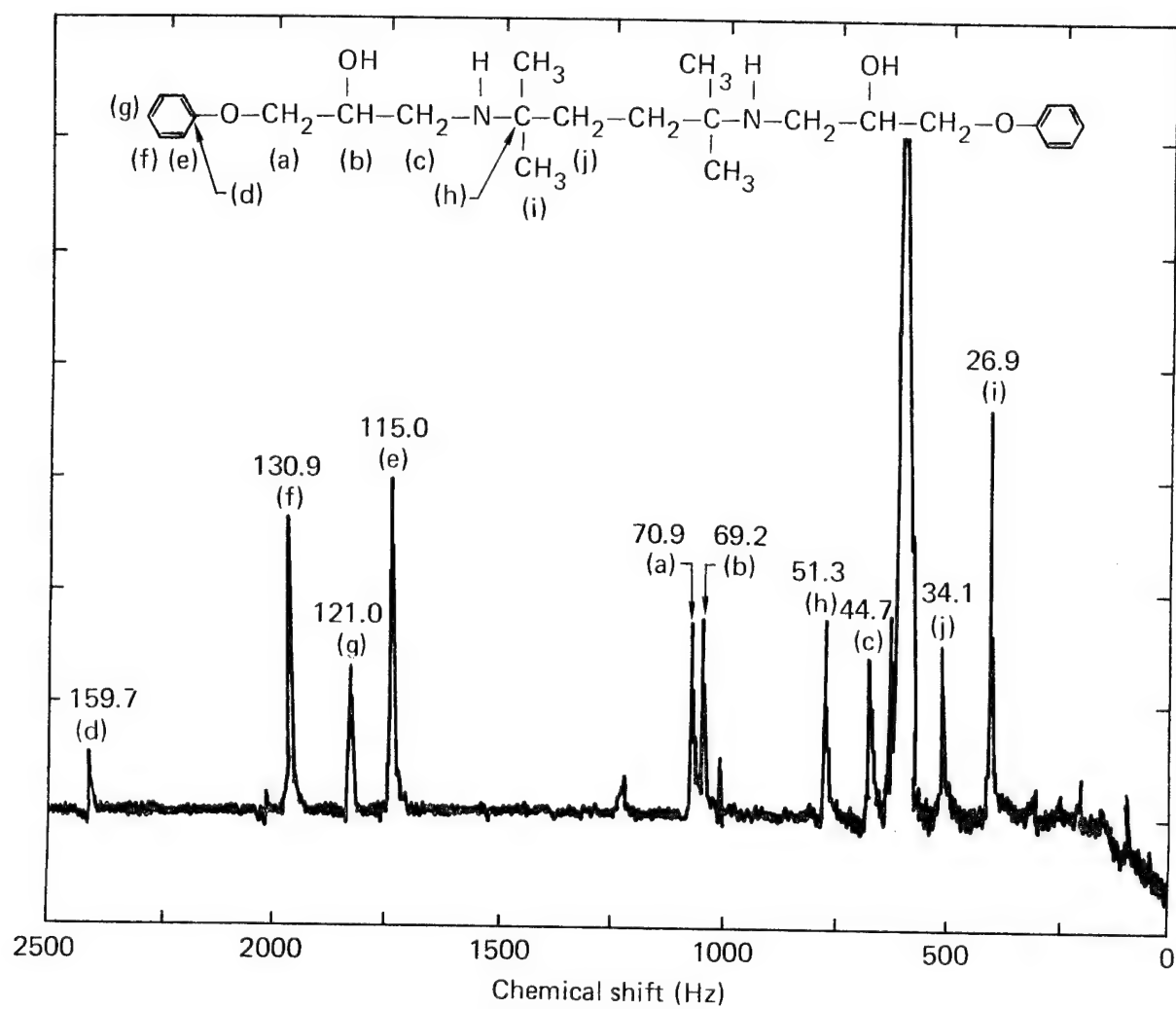
Fig. 5. Carbon-13 NMR peak heights at various times for DMHDA + PGE in DMSO at 100°C.

Fig. 6. Third-order kinetic plots of the reaction of DMHDA with PGE in DMSO at various temperatures: (a) 100°C, (b) 80°C, (c) 60°C, and (d) 46°C.

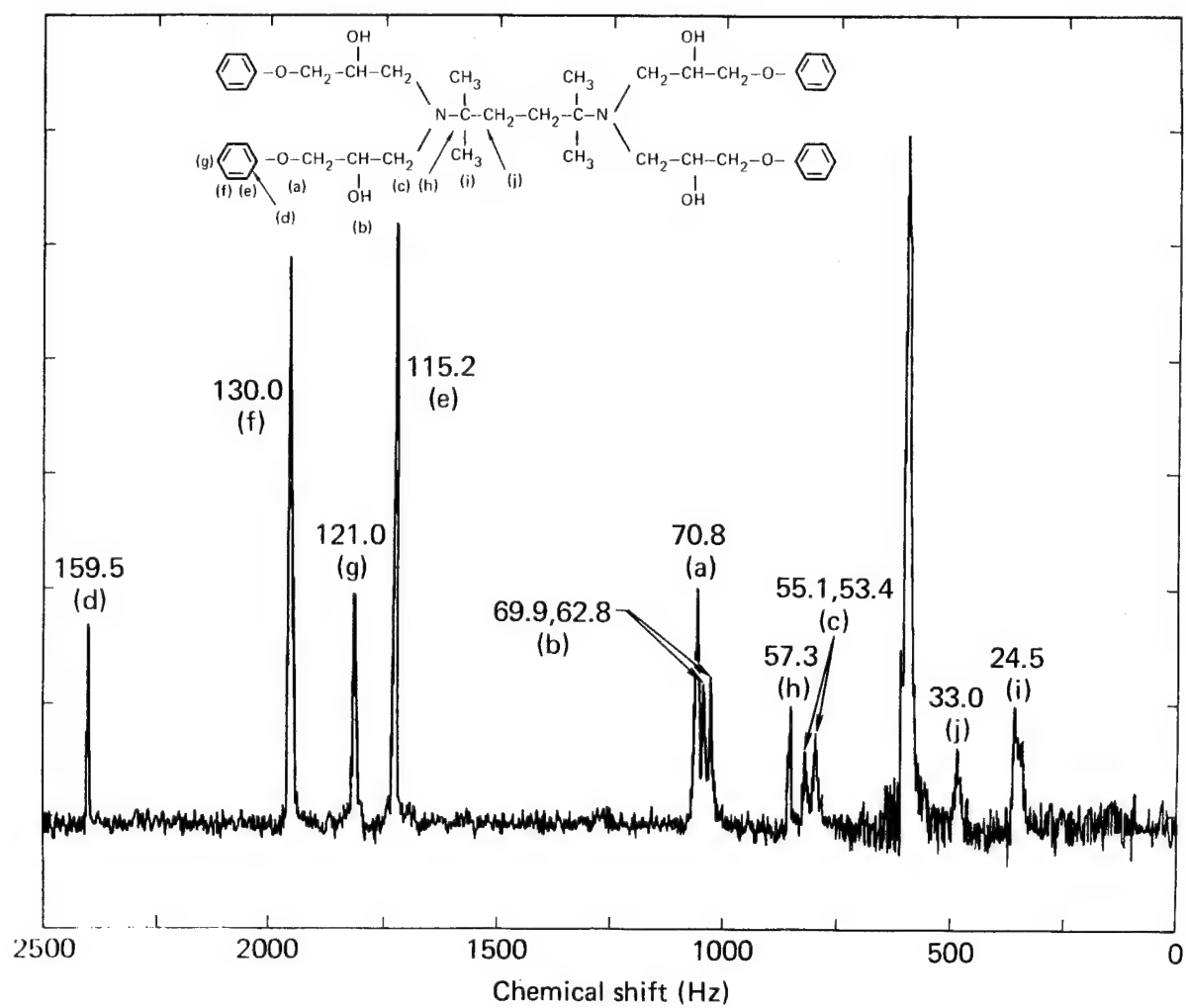
Fig. 7. Temperature dependence of rate constants for the reaction of DMHDA with PGE in DMSO solution.

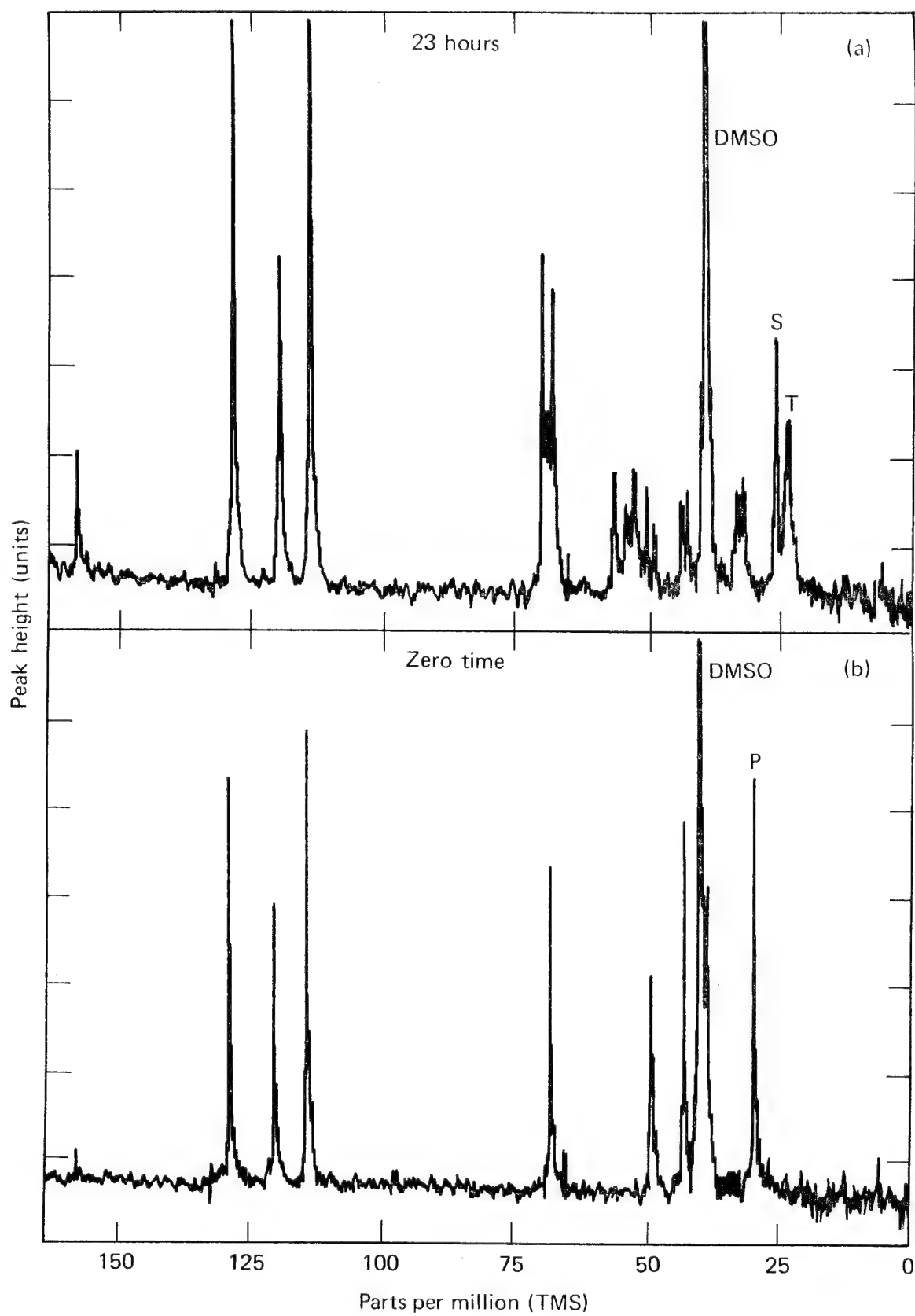


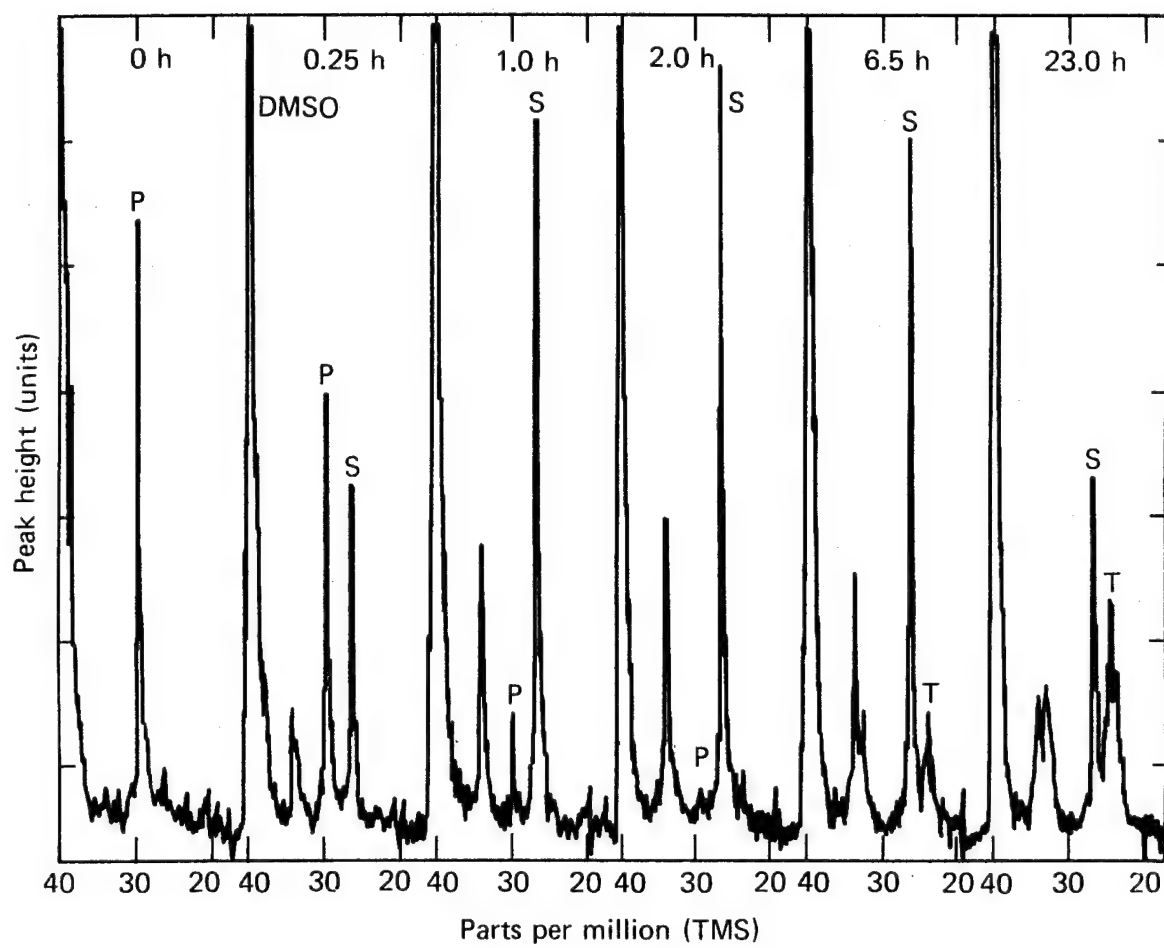
Rinde - Fig. 1

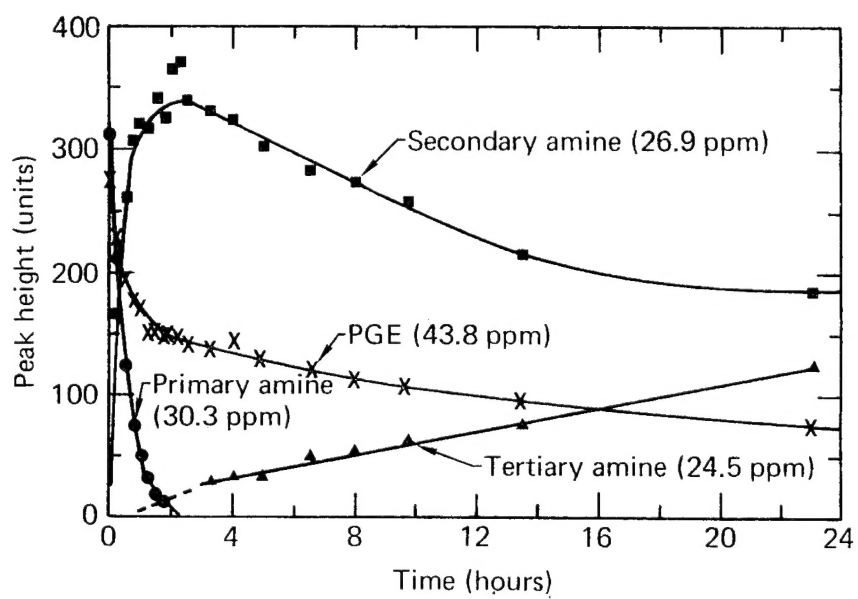


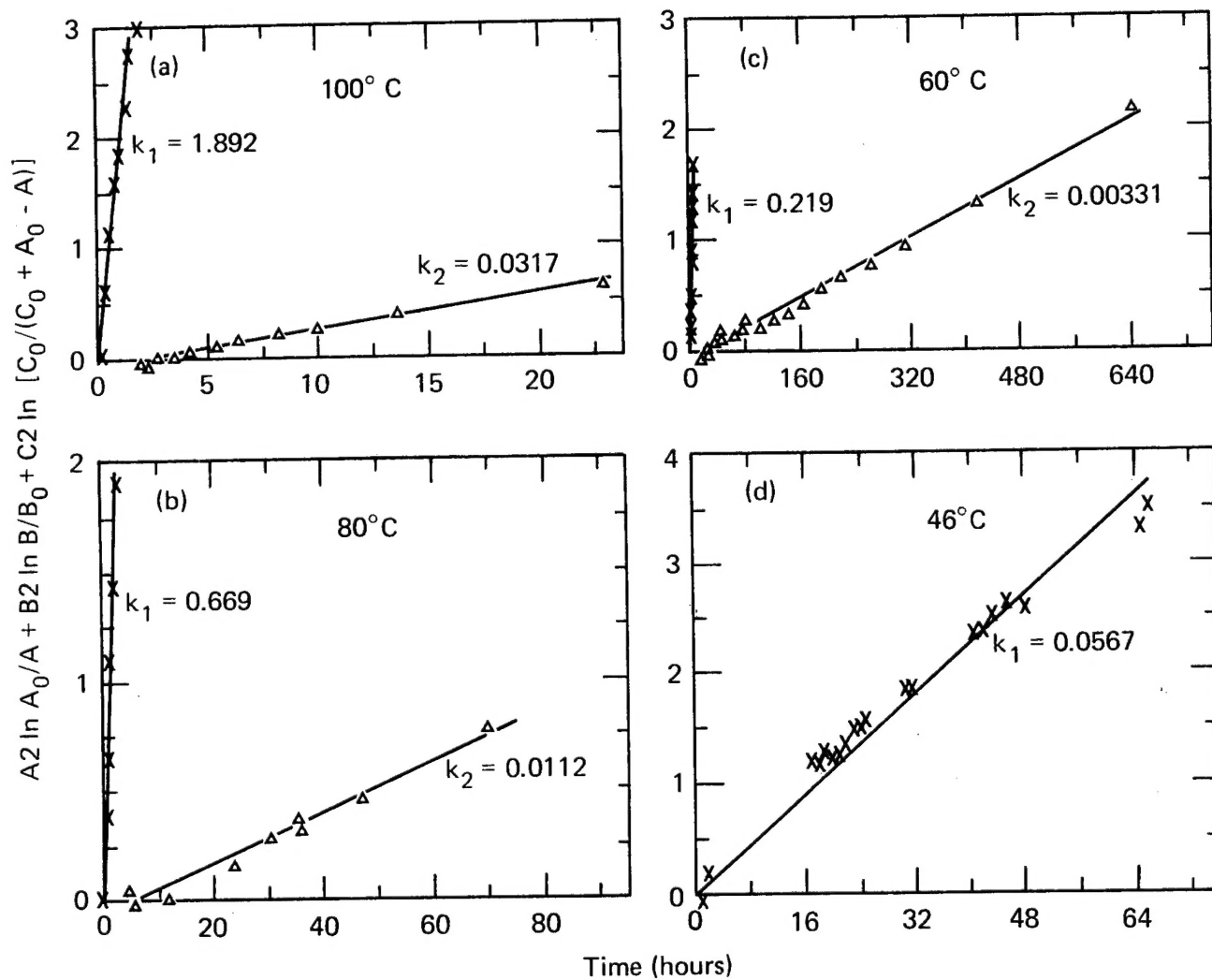
Rinde - Fig. 2a

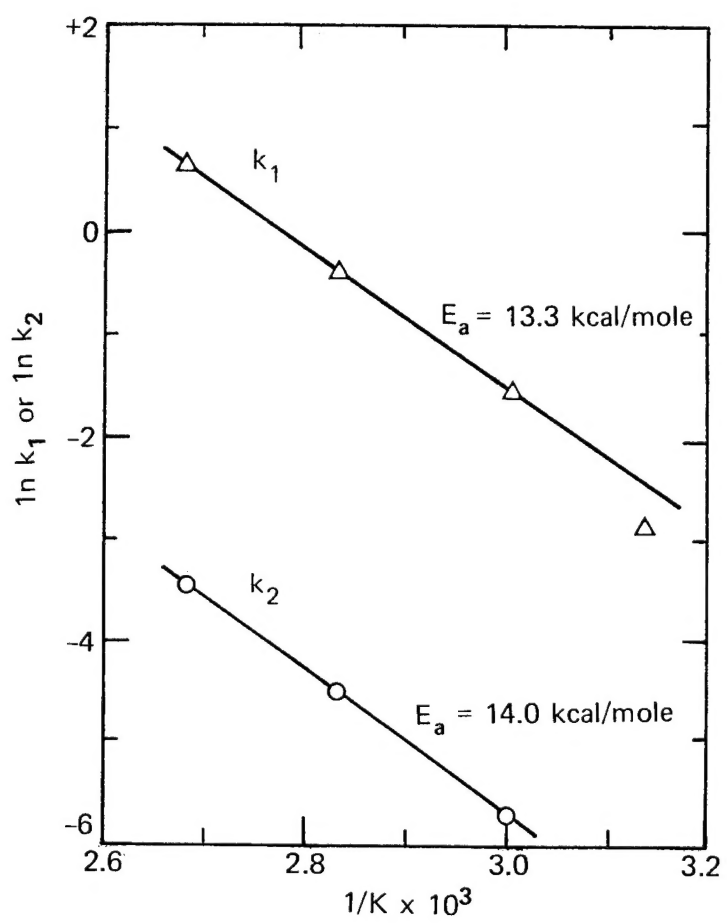












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